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(54) **Biaxially oriented polyester film.**

(57) The present invention relates to a biaxially oriented polyester film having improved friction coefficient and water resistance comprising a coating provided on at least one surface of the film.

The biaxially oriented polyester film is coated with water-soluble or water-dispersed resin compounds which are mixed water-dispersion waxy additives, styrene sulfonic acid compounds and inorganic fine particles, with the copolyester resins, on one or both sides.

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The present invention relates to a biaxially oriented polyester film having an improved friction coefficient and water resistance.

A polyester film, particulary biaxially oriented polyester film is widely used for film for graphic art, base film for photography, base film for magnetic tape, film for insulation, film for wrapping materials, film for agriculture, etc. because of the excellent transparency, dimensional stability, mechanical properties, electrical properties, heat resistance and chemical resistance thereof.

However, in spite of properties, polyester film has many defects during film-forming processes and other processing steps. For example, if the processing speed is increased in printing process or coating process, etc. many scratches are generated on the film surface owing to the rubbing against the roll and if the processing conditions are poor, the run ability and wind ability are degenerated because of the increase of friction coefficient.

The prior methods for improving the friction coefficient of the polyester film include the particle addition method which the inert fine particles are added during polyesterification and the precipitate out method induced from the ester ion exchange catalyst residue during polyesterification. However, these methods are effective to decrease a friction coefficient, but generate voids in film. This problem is to be a serious obstruction in microfilm and film for photography which are required an excellent transparency.

In the meantime, the polyester films, which are coated with copolyester resins dissolved or dispersed in water, have a bad water resistance and thereby are generated problems of the moisture absorption of coated layer, blocking property caused swelling and increase of turbidity during film-forming processes and other processing steps. The prior method for improving a water resistance includes a method which reactive compounds such as block polyisocyanates, vinyl compounds, methylolized or alkylolized urea compounds, melamine compounds, acrylamide compounds, epoxy compounds, etc. as cross-linking agents and inert fine particles are added. However, such cross-linking agents have defects that the coating property is poor when the solution property is different from the resins and/or solvents are used, and the transparency is worse after dryness. Then, in order to improve the coating property separate suface active agent is added, the transparency, friction coefficient, adhesion, water resistance ect. are impaired. Further, the inert fine particles are added, the friction coefficient and water resistance are improved, but the transparency is worse.

Accordingly, it is an object of the present invention to provide a biaxially oriented polyester film having an improved coefficient friction and water resistance by forming a coating layer which water-soluble or water-dispersed resin compounds are coated on one or both side of the polyester film.

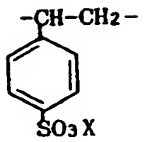
The present invention is characterized by biaxially oriented polyester film having an improved a friction coefficient and water resistance by coating the water-soluble or water-dispersed resin compounds which are mixed water-disperion waxy additive, styrene sulfonic acid compounds and inorganic fine particles with the copolyester resin, on the one or both side of the polyester film.

The copolyester resins employed in the present invention is water-soluble or water-dispersed resin having sulfonic acid salt group and it has ester bonds which obtained by polycondensation of dicarbonic acid and diol in the polymer main chain.

For example, the dicarbonic acid components of the polyester are terephthalic acid, isophthalic acid, adipic acid, 5-sodium sulfo isophthalic adid, trimellitic acid, trimellitic anhydride, phthalic anhydride, sebacic acid, etc. and diol components are ethylene glycol, 1,4-butandiol, propylene glycol, neopentyl glycol, 1,6-hexanediol, diethylene glycol, triethylene glycol, polyethylene glycol, polypropylene glycol, etc. To obtain aqueous polymer, 5-sodium sulfo isophthalic acid components or their salt group should be included in amount of 2~20mol% to the aromatic dibasic acid or ester-forming derivatives thereof. If the amount is less than 2mol%, an water-solubility or water-dispersion property of polymer is not enough and if the amount is more than 20mol%, a water-resistance of the film surface is lowered after coating and the films are easily adhered each other due to moisture absorption. The added amounts of the aromatic dicarbonic acid contained in the dicarbonic acid components of the polyester resin are preferably 50~100mol% because the extent raise the softening point of the polyester resins and increase an adherence property.

The water-dispersion waxy additive employed in the present invention are preferably polyethylen wax and polypropylene wax and preferable molecular weight is 500~50,000. The added amount of the wax is 0.1~20wt%, preferably 1~10wt% to the solid content of the copolyester resins. If the added amount is less than 0.1wt%, the friction coefficient is increased and if the amount is more than 20wt%, the friction coefficient is decrease but the water resistance is worse.

The styrene sulfonic acid compounds used in this invention are the polymer containing sulfonic acid having $-SO_3X$ group and/or sulfonic acid salt group thereof, especially one represented as following formula:



(Wherein, X is H^+, Li^+, Na^+, K^+, NH_4^+, etc.)

Also, the styrene sulfonic acid compound is preferably a polymer having over 1,000 of average molecular weight, more preferably over 10,000 and the added amount is 0.01~15wt%, preferably 0.1~10wt% to the solid content of the copolyester resins. When the used amount is below 0.01wt%, the water resistance is not enough and when the used amount is over 15wt% , the surface properties such as transparency and coating property are lowered.

In the present invention, the representative examples of the used inorganic fine particles which are substantially inactive are titanium oxide, silicon oxide, calcium carbide, kaolin, calcium fluoride, alumina, barium sulfate, zirconium, mica, calcium phosphate, etc. and it is desirable to use the particles of inorganic colloidal state, especially spherical shape particles. The average particle diameter of the inorganic fine particles is preferably 5~5,000nm and two types of particles having 5~110nm of the particle diameter (A) and 120~5,000nm of the particle diameter (B) preferably 30~90nm (A) and 140~500nm (B) respectively should be used.

Further, the use ratio (A):(B) of the these particles is 0.1:1~1:5, preferably 0.4:1~1:2. If the average particle diameter and the added amount of the inorganic fine particles are deviated from the above extents, the transparency, coefficient friction, water resistance and so on are impaired. According to the present invention, the positive-ionic, negative-ionic or non-ionic surface active agents can be used and it is desirable to use the non-ionic surface active agent to increase the coating property of the water-soluble or water-dispersed resin compounds.

Also, anti-foaming agents, thickeners, antioxidants, ultra- violet ray absorbents, pH control agents etc. can be added in the water-soluble or water-dispersed resin compounds.

The copolyester resins are prepared into water solution or water-dispersion solution, by using the water-soluble organic compounds or hot water and as the water-soluble organic compounds, an alcohol, ether, ketone, more particularly, methanol, ethanol, isopropanol, n-butanol, ethylen glycol, propylene glycol, methyl cellosolve, ethyl cellosolve, n-butyl cellosolve, methyl ethyl ketone etc. can be used.

It is desirable that the polyester films employed in the present invention have below 0.03μm, preferably 0.015μm of the surface roughness measured by centerline average roughness and below 10.0, preferably 2.0 of the turbidity.

The films having 30~200μm of thickness can be used.

The water-soluble or water-dispersed resin compounds can be prepared by adding the water-dispersion waxy additives (A), styrene sulfonic acid compounds (B) and inorganic fine particles (C) to the copolyester resins and the mixture ratio (A):(B):(C) is 0.1~20wt% : 0.01 ~ 15wt% : 0.01~5wt% by solid content to the solid contents of the copolyester resins.

The solid contents of water-soluble or water dispersed resin compounds in this invention is preferably below 20wt%, more preferably 1~8wt% and the viscosity is below 100 cps, preferably below 20 cps.

The methods of coating can he applied the conventional methods and the coating amount is 0.001~2g/m^2, preferably 0.008~0.5g/m^2 for the obtained film.

The biaxially oriented polyester film of the present invention can be widely used for basic materials, for microfilm, label, OHP, film for vacuum evaporation, film for lamination etc. because of the excellent surface properties and water resistance thereof.

The present invention will further be illustrated by the following examples, in which the properties of the films were measured as follows;

(1) Turbidity

Turbidity was measured by Automatic NDH-20 of NIPPON DENSHOKU CO, LTD. and was recorded as (scattering light/total light) X 100.

(2) Friction Coefficient

Coefficients of static friction and kinetic friction were measured by the Slippery-meter manufactured by

Orient Tester Co., Ltd. according to the method of ASTM D-1894 under a load of 200g.

(3) Adhesion

Pink lacquer as a resin for evaluation was coated on the film coated resin, and dried and then cracked for lattice at interval of 1mm and attached fully with the cellophane adhesive tape (3M Inc. 610) to not flowin an air, and seperated suddenly from film coated resin. Then, the numbers of part which not seperated in 100 of lattices at interval of 1mm were counted and represented percentage.

(4) Water Resistance

The biaxially oriented polyester film which the resin is coated on the both surface was digested for 30 minute in 50 °C of warm water, naturally dried, and evaluated the turbidity compared with film before treatment. The results of the evaluation were indicated as follows;
below 0.4 of turbidity increase value : O (favorable)
0.5~0.7 of turbidity increase value : ▲ (little bad)
over 0.8 of gurbidity increase value : X (bad)

EXAMPLE 1

(I) Preparation of a water-soluble polyester resin .

The mixture of 49mol% of dimethylterephthalate, 43.5mol% of dimethylisophthalate and 7.5mol% of 5-sodiumsulfoisophthalic acid as dicarbonic acid component, ethylene glycol and diethylene glycol were reacted, and the polyester having 64 °C of a glass transmission temperature was obtained.

(II) Preparation of a biaxially oriented polyester film.

Two types of inorganic fine particles having 5~110nm(A) and 120~5,000nm(B) of average particle diameter, were used respectively.

A polyethylene terephthalate having an intrinsic viscosity of 0.66cps in O-chlorophenol at 25 °C was melted and extruded by extruder, and cooled suddenly on the drum of 40 °C to obtain an unstreched film having 650μm of thickness. And then the unstreched film was streched on the 95 °C of metallic roll in the moving direction of the film to 3.6times to original length.

Seperately, the resin compounds having 5wt% of solid content was prepared by adding 5wt% of water-dispersion waxy additive, 4wt% of styrene sulfonic acid compound, 1.0wt% of above (A) and (B) respectively as inorganic fine particles and 1.0wt% of NS-208.5 manufactured by Japan Oil and Fats Co., Ltd. as 0.5wt% of non-ionic surface active agent to 5wt% of water-soulble copolyester resins prepared above (I).

This resin compounds were coated on the above streched film and the coated film was streched to 3.6 times at temperature of 105 °C and heat treated at temperature of 220 °C, thereby 50μm of thickness of biaxially oriented polyester film having 0.05μm of thickness of coating layer was obtained.

In the obtained film, the properties were measured and the results are shown in TABLE 1.

EXAMPLE 2

Example 1 was repeated except that 10wt% of the waxy additive was used and styrene sulfonic acid compounds and inorganic fine particles were not added, thus the biaxially oriented polyester film was obtained.

The properties of the obtained film are shown in TABLE 1.

EXAMPLE 3

Example 1 was repeated except that 5.3wt% of styrene sulfonic acid compound was used and waxy additive and inorganic fine particles were not added, thus the biaxially oriented polyester film was obtained.

The properties of the obtained film are shown in TABLE 1.

EXAMPLE 4

Example 1 was repeated except that 2wt% of styrene sulfonic acid compound was used and waxy additive and inorganic fine particles were not added, thus the biaxially oriented polyester film was obtained.

The propertics of the obtained film are shown in TABLE 1.

EXAMPLE 5

Example 1 was repeated except that 20wt% of waxy additive was used and styrene sulfonic acid compound and inorganic fine particles were not added, thus the biaxially oriented polyester film was obtained.

The properties of the obtained film are shown in TABLE 1.

COMPARATIVE EXAMPLE 1

Example 1 was repeated except that waxy additive, styrene sulfonic acid compound and inorganic fine particles were not used, thus the biaxially oriented polyester film was obtained.

The properties of the obtained film are shown in TABLE 1.

COMPARATIVE EXAMPLE 2

Example 1 was repeated except that WR-901 manufactured by NIPPON GOSEI CO., LTD. was used instead of the water-soluble copolyester resin prepared above (I) and waxy additive, styren sulfonic acid compound and inorganic fine particles were not added, thus the biaxially oriented polyester film was obtained.

The properties of the obtained film are shown in TABLE 1.

TABLE 1.

	TURBIDITY	COEFFICIENT		ADHESION	WATER RESISTANCE
		μS	μK		
EXMPLE 1	0.4	0.35	0.29	100/100	O
EXMPLE 2	0.4	0.36	0.30	100/100	▲
EXMPLE 3	0.4	0.43	0.38	100/100	▲
EXMPLE 4	0.4	0.47	0.39	100/100	▲
EXMPLE 5	0.4	0.30	0.26	100/100	▲
COMPARATIVE EXMPLE 1	0.4	0.50	0.42	100/100	X
COMPARATIVE EXMPLE 2	0.4	0.59	0.56	100/100	X

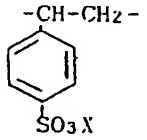
Claims

1. A biaxially oriented polyester film having at least one surface layer coated with water-soluble or water-dispersed resin compounds comprising water-soluble copolyester resins, water-dispersion waxy additives, styrene sulfonic acid compounds and inorganic fine particles.

2. The polyester film according to claim 1, wherein water-soluble copolyester resins comprise over 85mol% of aromatic dicarbonic acid and below 15mol% of dicarbonic acid containing sulfonic acid alkali metallic salt group to amount of total dicarbonic acid component and have 45–75 °C glass transmission temperature.

3. The polyester film according to claim 1, wherein water- dispersion waxy additive is polyolefin compound and have 500– 50,000 of molecular weight.

4. The polyester film according to claim 1, wherein styrene sulfonic acid compound is polymer having sulfonic acid containg -SO_3X group and/or salt thereof and represents as following formula.



(Wherein, X is H^+, Li^+, Na^+, NH_4^+, etc.)

5. The film according to claim 1, wherein inorganic fine particles are substantially inactive and are spherical shape which average particle diameters are 5~110nm(A) and 120~5,000nm(B) respectively and the used ratio of particles (A):(B) is 0.1:1~1:5.

6. The film according to claim 1, wherein water-soluble or water-dispersed resin compounds are composed of 0.1~20wt% of waxy additive, 0.01~15wt% of styrene sulfonic acid compound and 0.01~5wt% of inorganic fine particles.